Characteristics of the HCHO oxidation reaction over Pt/TiO$_2$ catalysts at room temperature: The effect of relative humidity on catalytic activity

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A R T I C L E I N F O

A B S T R A C T

This study investigated the effect of relative humidity on HCHO oxidation at room temperature over Pt/TiO$_2$ catalysts prepared by wet impregnation. Atmospheric moisture acts as a promoter that increases the catalytic activity of the formaldehyde oxidation reaction. From DRIFTs, it was confirmed that the excellent performance was caused by the hydroxyl group resulting from the presence of moisture. The hydroxyl group on the catalyst surface could be recovered by atmospheric oxygen. Surface –OH or lattice oxygen could be used for adsorption and conversion of HCHO into formate even if atmospheric oxygen was not present. Adsorbed formate could be oxidized into CO$_2$ and H$_2$O using the surface –OH or –OH from H$_2$O. The Pt/TiO$_2$ catalyst prepared in this study showed excellent activity and could completely remove HCHO at room temperature. It was also confirmed that HCHO could be oxidized by our catalyst even when using a small quantity of Pt (0.1 wt%).

1. Introduction

Carbon monoxide (CO), nitrogen dioxide (NO$_2$), ozone (O$_3$), particulate (PM10), asbestos, volatile organic compounds (VOCs), radon (Rn) and formaldehyde (HCHO) are indoor air pollutants that can severely affect health. Among these harmful substances, formaldehyde is the most toxic, as it has a negative influence on genetic material, respiratory tracts and cutaneous covering and strongly affects the central nervous system. Accordingly, some residents of new apartments suffer from various health complaints, including headaches, dizziness, sickness, sleepiness, eye irritation, decreased concentration, atopic dermatitis, Sick Building Syndrome (SBS), Sick House Syndrome (SHS) and Multiple Chemical Sensitivity (MCS) [1–3].

Many physico-chemical processes exist in HCHO removal technology, such as adsorption onto activated carbon (AC), photocatalytic oxidation (PCO) and catalytic oxidation [4]. Among these techniques, catalytic oxidation is a promising technology for the remove of formaldehyde because formaldehyde can be oxidized over catalysts at a lower temperature than that used for thermal oxidation [5]. For example, formaldehyde was completely oxidized over a Pd-Mn/Al$_2$O$_3$ catalyst at approximately 363 K [6] and ceramic supported Pt catalyst at approximately 423 K [7].

In this respect, supported precious metals (Au, Ru, Pd, Ag, and Pt) have been proven to be effective catalysts for the removal of formaldehyde [8–12]. Recently, researchers have performed the complete removal of formaldehyde at room temperature using a catalyst. Zhang et al. [8,12] described a formaldehyde removal mechanism using a Pt/TiO$_2$ catalyst at room temperature. Tang et al. [10] performed a study of the catalytic activity at room temperature by reducing a Pt/MnO$_x$-CeO$_2$ catalyst and examining the importance of oxygen when removing HCHO. However, the influence of moisture on formaldehyde oxidation by noble metal-supported catalysts has not been investigated.

The moisture in indoor air is one of the major causes of the dramatic loss of catalytic activity that occurs through strong adsorption on active sites, especially at low temperatures [13]. There are several reports, sometimes contradictory, on the effective of moisture on catalytic oxidation. The presence of water was found to suppress the catalytic activity of a TiO$_2$ supported gold catalyst [14]. Water adsorbed on TiO$_2$ is known to adsorb both associatively and dissociatively (as –OH) on reduced Ti cations and to oxidize the surface, which blocks the unsaturated coordination sites on the TiO$_2$ surface [15]. However, according to the results

from a CO oxidation reaction using an Au/Al_2O_3 catalyst based on partial water pressure, Ojeda et al. [16] claimed that an appropriate partial water pressure existed and that water was the essential factor in the reaction. According to the results of oxidation experiments using a Pd catalyst at room temperature based on on–off of the water, Shen et al. [17] reported that with no water injection there was low activity, but with injection, there was 100% activity. According to the results obtained by conducting a CO oxidation reaction at room temperature based on a pretreatment condition, Zou et al. [18] reported that activity degradation occurred with pretreatment at high temperatures and that this activity varied based on the degree of participation of the water in these reactions.

Hence, it is important to understand the effects of feed composition humidity on the catalytic activity, the reaction pathway and the product distribution of CO_2. In our present study of the catalytic oxidation of formaldehyde, we used a Pt/TiO_2 catalyst, which has shown high activity at room temperature [19]. To increase the oxidation of formaldehyde at room temperature, metallic platinum oxide was applied upon catalyst reduction. The aim of the present work was to investigate the characteristics of the HCHO oxidation reaction over Pt/TiO_2 catalysts at room temperature. Our study focused particularly on the effect of relative humidity on the catalytic activity. The influence of humidity on formaldehyde oxidation was examined by performing the experiment in the presence or absence of humidity. The catalyst was prepared by a formula for differentiating the Pt loading %.

2. Experiments

2.1. Catalyst preparation

The catalyst used in this study was a Pt/TiO_2 catalyst, which was manufactured by loading the platinum onto commercialized TiO_2 supports. The TiO_2 supports used were divided into two types: commercial TiO_2(A) powder (Millennium Chemical Co., 100% anatase phase) and commercial TiO_2(B) powder (Wako Pure Chemical Co., 90% anatase phase and 10% rutile phase). The Pt/TiO_2 catalyst, which was loaded by the calculation of different weight percentages (0.01, 0.1, 0.5 and 1 wt%) of platinum, was marked "C" if it was calcined in the final process of the manufacturing and "R" if it was reduced. The catalyst preparation method used in this study was the wet impregnation method. First, the platinum content in TiO_2 was calculated based on the desired composition; then, this amount of platinum chloride [$PtCl_4$; Aldrich Chemical Co.] was dissolved in distilled water that was heated to 60 °C in order to increase the solubility of the metal. The calculated amount of TiO_2 was combined with the solution by gradual addition with stirring. This mixed solution, which was in a slurry state, was then stirred for more than an hour before the water was evaporated at 70 °C using a rotary vacuum evaporator (Eyela Co. N-N series). After the water was evaporated, the samples were dried for an additional 24 h in a 103 °C dry oven to remove the residual water. Then, in order to remove the residual chlorine, the sample was thermally treated in air for 3 h at 300 °C. In the last step, the sample was calcined in air for 4 h at 400 °C. The final catalyst was prepared by reducing the calcined catalyst with hydrogen for 4 h at 600 °C [19].

2.2. Catalytic activity tests

The fixed bed reactor used to examine the reactive properties of formaldehyde when oxidized at room temperature was composed of a gas injection section, an oxidation tower section, a reactor section, and a section for analyzing the reaction gas. We used paraformaldehyde, which was injected by vaporization of the paraformaldehyde through supplying a specific amount of

carrier gas to the impinger [20–22]. After the impinger containing the paraformaldehyde was fixed in a constant-temperature tank maintained at 22 °C, HCHO was injected by vaporization of the paraformaldehyde by supplying a specific amount of carrier air to the impinger. The temperature of the constant-temperature tank was maintained so that the concentration of HCHO was 22 (±2) ppm in the generated gas. In addition, moisture was supplied by injecting air containing moisture using a bubbler; in order to maintain a constant supply rate, we circulated water at a constant temperature (25 °C) using a circulator around the bubbler in the form of a double jacket. The relative humidity was 30% and 54%, and this value was measured using humidity equipment (CENTER 310 series, center technology Co.). The reactor was a continuous-flow-type fixed bed reactor made of a quartz tube with an internal diameter of 8 mm and a height of 600 mm, and quartz wool was used to fix the catalytic bed. Approximately, 0.25 g of catalyst (40–50 mesh) was used for each reaction run. Under ambient conditions, the total flow rate was 500 cm³/min, and the gas hourly space velocity (S.V.) was 60,000 h⁻¹. In addition, the space velocity (60,000–360,000 h⁻¹) was controlled by adjusting the amount of catalyst.

The temperature of the reactor was controlled by filling the outside of the reactor with water, and a K-type thermocouple was installed to measure the temperature.

When measuring the concentration of reactants and products, CO and CO_2 were analyzed using a non-dispersion infrared gas analyzer (ZKJ-2, Fuji Electric Co. range of 0–100 ppm), and HCHO was analyzed using a detector tube (91, Gas Tec. Co.). A catalytic oxidation tower (Pt/TiO_2 at 300 °C) was used to measure the concentration of CO_2 generated from the injected HCHO. One mole of HCHO was oxidized to produce 1 mol of CO_2. The catalytic oxidation tower was designed to achieve the complete oxidation of HCHO into CO_2, and in order to confirm complete oxidation, we analyzed the concentration of unreacted HCHO at the rear end of the catalyst tower using detector tubes (CO, HCHO, CH_3OH and HCOO). The injection of paraformaldehyde through vaporization generates HCHO, and HCHO is oxidized to produce CO_2. Thus, in the present study, the CO_2 concentration was measured by a NDIR analyzer (CO and CO_2) after the paraformaldehyde was vaporized and traveled through the oxidation catalyst tower. This was taken as the inlet concentration. The CO_2 concentration was also measured after passing through the prepared Pt/TiO_2 catalyst bed reactor at 25 °C and considered the outlet concentration.

Using the concentrations of the gases at a steady state, the conversion is calculated according to the following equation:

$$\text{HCHO conversion} = \frac{C_{\text{after reaction } CO_2}}{C_{\text{oxidation tower } CO_2}} \times 100 \qquad (1)$$

2.3. Catalyst characterization

The BET surface areas of the catalysts were measured using an ASAP 2010C (Micromeritics Co.). The specific surface area was estimated using the BET method, and the pore size distribution was calculated using the Barrett–Joyner–Halenda method, which calculates the pore size based on the adsorption layer thickness in relation to the pressure and the average radius of the meniscus, as obtained using the Kelvin method. Each sample was then analyzed after degassing in a vacuum at 110 °C for 3–5 h.

The X-ray diffraction measurements were carried out using Cu Kα (λ = 1.5056 Å) radiation. The catalysts were run at 2θ ranging from 10° to 80° with a step size of 0.1° and a time step of 1.0 s using a PANalytical X'Pert Pro MRD.

In situ DRIFTs analysis was used in this study, performed with an FT-IR 660 Plus (JASCO Co.), and a DR (Diffuse Reflectance) 400 accessory was used for the solid reflectance analysis. The CaF_2 window
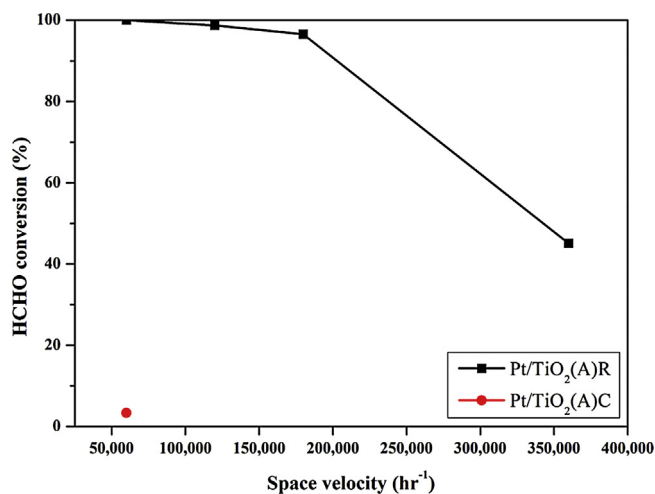
Fig. 1. Catalytic activities of the Pt/TiO$_2$(A) catalysts (*Reaction conditions*: Inlet HCHO 24 ppm, 21% O$_2$/N$_2$, temperature 25 °C, R.H. 54%, S.V. 60,000–360,000 h^{-1}).
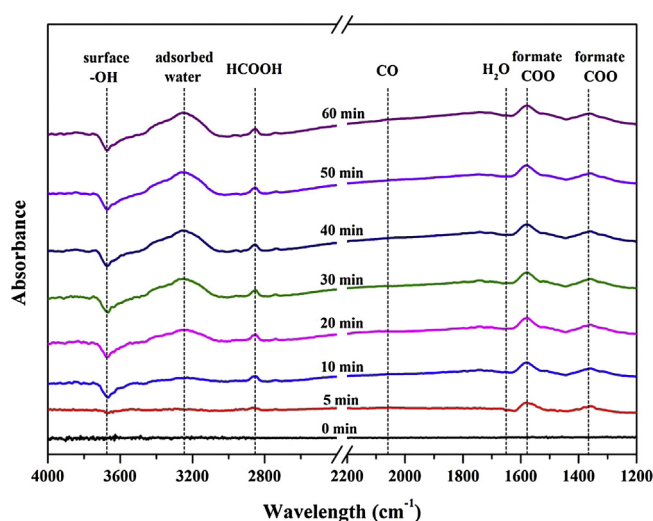

Fig. 2. Dynamic changes of the in situ FT-IR spectra of the Pt/TiO$_2$(A)R catalyst as a function of time in a flow of HCHO + N$_2$ at room temperature (*Reaction conditions*: Inlet HCHO 24 ppm, total flow rate 50 cm^3/min).

was used as a plate for DR measurement, and spectra were collected using a mercury cadmium telluride (MCT) detector. All of the catalysts used in the analysis were ground using a rod in the sample pan of an in situ chamber with a temperature controller installed. To exclude the influence of moisture and impurities, the sample was preprocessed with Ar at a rate of 50 cm^3/min at 150 °C for 1 h, and then the vacuum state was maintained using a vacuum pump. To collect the spectra of the catalyst, a single-beam spectrum of the preprocessed sample was measured as background, and all analyses were performed by auto scanning at a resolution of 4 cm^{-1}. We used paraformaldehyde for the HCHO injection, which was injected by vaporization of the paraformaldehyde by supplying a specific amount of carrier gas to the impinger.

An ESCALAB 210 (VG Scientific) was used for X-ray photoelectron spectroscopy (XPS) analysis, and monochromatic Al Kα (1486.6 eV) was used as the excitation source. After complete removal of the moisture in the catalysts by drying at 100 °C for 24 h, the catalysts were analyzed without surface sputtering and etching, so that the degree of vacuum in the XPS equipment was maintained at 10^{-6} Pa. The spectra were analyzed using XPS PEAK software (version 4.1). The intensities were estimated from the integration of each peak, subtraction of the Shirley background, and fitting of the experimental curve to a combination of Lorentzian and Gaussian lines of various proportions. All binding energies were referenced to the C 1s line at 284.6 eV. Binding energy values were measured with a precision of ±0.3 eV.

The characterization of the catalysts in terms of their dispersion and crystallite size was measured using chemisorption (Auto-Chem 2920, Micromeritics). The catalyst sample was activated in a helium flow at 300 °C for 30 min, cooled to 25 °C and then saturated with pulses of carbon monoxide (CO/He = 10/90 as vol.%). The amount of carbon monoxide adsorbed was calculated from the amount removed due to chemisorption.

3. Results and discussion

3.1. Physicochemical characteristics of the Pt/TiO$_2$ catalysts

The experiments were performed using catalysts pretreated under calcination and reduction conditions with various space velocities to examine the effects of moisture on the formaldehyde oxidation activity of Pt/TiO$_2$ catalysts. The results are shown in Fig. 1. In the case of the Pt/TiO$_2$(A)R catalyst, which showed excellent activity at room temperature, 100% of the formaldehyde

was removed at S.V. 60,000 h^{-1}, and 96% excellent activity was maintained at S.V. 180,000 h^{-1}. In addition, there was a 45% formaldehyde oxidation activity at S.V. 360,000 h^{-1}. However, the Pt/TiO$_2$(A)C catalyst had a very low activity at S.V. 60,000 h^{-1}. The surface area and CO chemisorption properties of the Pt/TiO$_2$(A) catalysts were examined in order to understand these differences in activity. The results are shown in Table 1, which indicates that the surface areas of the Pt/TiO$_2$(A)C and Pt/TiO$_2$(A)R catalysts were 135 and 107 m^2/g, respectively. The surface area of Pt/TiO$_2$(A)R catalyst was reduced compared to that of Pt/TiO$_2$(A)C catalyst because of the thermal treatment at high temperature. The surface area of the Pt/TiO$_2$(A)C-600 catalyst was 104 m^2/g, as shown in Table 1. The decrease in the surface area was due to the thermal treatment, not the reduction treatment by hydrogen. If thermal treatment was performed at a high temperature, the catalyst and activity were both degraded. However, the results of this study indicate that the Pt/TiO$_2$(A)R catalyst showed greater activity than the Pt/TiO$_2$(A)C catalyst. A high quantity of CO uptake was observed for the Pt/TiO$_2$(A)R catalyst. In addition, the Pt/TiO$_2$(A)R catalyst showed a high dispersion of metallic Pt species, and the metal surface area was large. This was thought to be caused by the strong metal support interaction (SMSI) effect of TiO$_2$ and the platinum metal. According to Kim et al. [23–25], TiO$_2$ could be reduced and was shown to produce the SMSI effect with Pt. The SMSI effect, which was caused by a strong interaction between the reduced Ti^{3+} sites and Pt, could produce reduction sites on the TiO$_2$ support. It was reported that the metal was widely dispersed, and the activity of the catalyst was increased if the affinity of the metal and the support was strong. The Ti2p peak of Pt/TiO$_2$(A)R by XPS was shifted to a lower energy level compared to that of the Ti2p peak of Pt/TiO$_2$(A)C (not shown here). This means that the electron moved to the metal from the support [26].

3.2. DRIFTs

In situ FT-IR analysis was performed to examine the role of moisture during the formaldehyde oxidation. Fig. 2 shows the changes in the peaks upon injection of HCHO + N$_2$ into the reactor containing the Pt/TiO$_2$(A)R catalyst at room temperature. The negative peak at 3674 cm^{-1} and the positive peak at 2860 cm^{-1} were observed 10 min following the injection of HCHO and N$_2$. In addition, a broad peak was observed at a wavelength between 3000 and 3500 cm^{-1}. These peaks show a tendency to gradually increase

Table 1
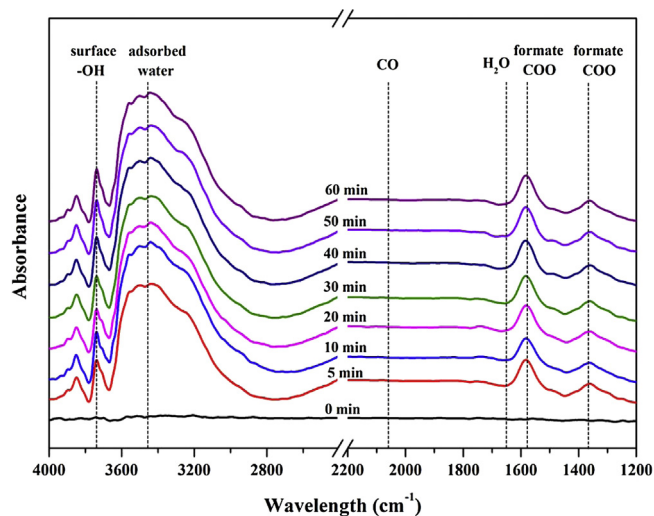The surface area and CO chemisorption properties of Pt/TiO_2 catalysts.

Catalyst	S_{BET} (m^2/g)	CO uptake (μmol/g)	Metal dispersion (%)	Metal surface area (m^2/g)
$TiO_2(A)$	288	–	–	–
$Pt/TiO_2(A)C$	135	0.30	0.59	1.45
$Pt/TiO_2(A)R$	107	18.24	35.38	47.88
$Pt/TiO_2(A)C-600^*$	104	0.21	0.41	1.02
$TiO_2(B)$	65	–	–	–
$Pt/TiO_2(B)C$	49	0.14	0.28	0.68
$Pt/TiO_2(B)R$	11	1.92	3.77	9.27

* $Pt/TiO_2(A)C$ was thermal treated in air for 1 h at 600 °C.

as the reaction time approaches 60 min. Additionally, the –COO peak was observed at 1570 and 1360 cm^{-1} [12]. Generally, peaks appearing at 3674 and 3747 cm^{-1} indicate that the hydroxyl group is on the catalyst surface [27], whereas peaks at 2860–2869 cm^{-1} indicate the presence of dioxymethylene (HCOOH) [20]. Additionally, some broader peaks at 3000–3500 cm^{-1} and strong peaks at 3455 and 1637 cm^{-1} were attributed to the O–H stretching vibration of water, the Ti–OH group, and hydrated species on the TiO_2 surface, respectively [28]. The results also showed that a broad peak was observed at a wavelength between 3000 and 3500 cm^{-1} because HCHO was oxidized into CO_2 and H_2O. Kim et al. [19] claimed that formate and CO peaks were observed in the HCHO + N_2 reaction, and the decrease of the CO peak was caused by lattice or adsorbed surface oxygen in the catalyst. In this study, moisture, which was a product of the HCHO oxidation, was observed by lattice or adsorbed surface oxygen. In addition, it was thought that the peak of the hydroxyl group (3674 cm^{-1}) on the surface of the catalyst was lower under conditions where oxygen and moisture were not supplied because surface–OH was an important factor participating in the reaction. Fig. 3 shows changes in the peaks upon injection of HCHO + N_2 + H_2O into the reaction with the $Pt/TiO_2(A)R$ catalyst. The decrease in the amount of surface –OH groups was small. In addition, a broad adsorbed water peak at 3000–3500 cm^{-1} was observed while a formate peak did not appear. In other words, the amount of surface –OH groups on the catalyst surface was not decreased by atmospheric H_2O, whereas the water adsorbed on the catalytic surface was increased. FT-IR analysis was performed using the $Pt/TiO_2(A)C$ catalyst with low formaldehyde oxidation activity in the presence and absence of H_2O. Fig. 4 shows the HCHO + N_2 reaction in the absence of H_2O, whereas Fig. 5 shows the results of the HCHO + N_2 reaction in the presence of H_2O. When Fig. 2 is
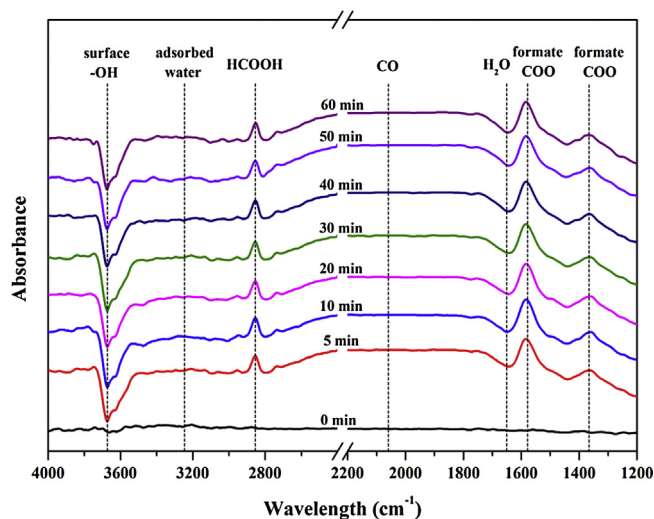
Fig. 4. Dynamic changes of the in situ FT-IR spectra of the $Pt/TiO_2(A)C$ catalyst as a function of time in a flow of HCHO + N_2 at room temperature (*Reaction conditions*: Inlet HCHO 24 ppm, total flow rate 50 cm^3/min).

compared with Fig. 4, an adsorbed water peak at 3000–3500 cm^{-1} is absent for the $Pt/TiO_2(A)C$ catalyst. Formaldehyde was reacted with oxygen to produce CO_2 and H_2O as byproducts. However, it was confirmed that H_2O was produced when formaldehyde was reacted with the $Pt/TiO_2(A)R$ catalyst in the absence of atmospheric oxygen (Fig. 2). This adsorbed water peak was produced by oxidizing formaldehyde. In other words, the H_2O peak was produced through the reaction of HCHO and N_2 by the reduced catalyst in which
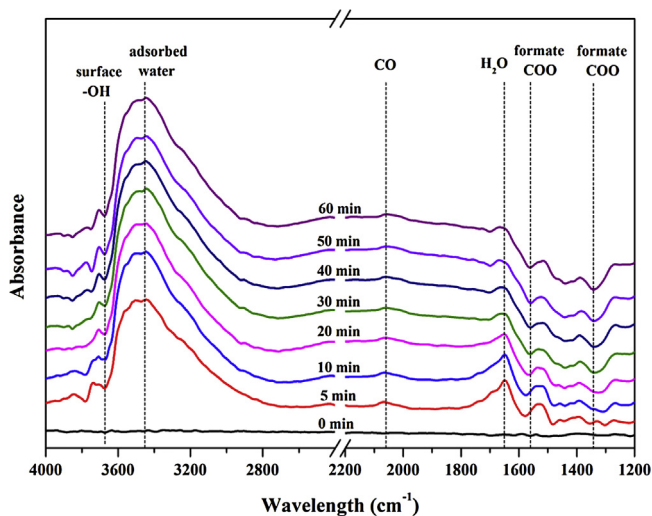
Fig. 3. Dynamic changes of the in situ FT-IR spectra of the $Pt/TiO_2(A)R$ catalyst as a function of time in a flow of HCHO + N_2 + H_2O at room temperature (*Reaction conditions*: Inlet HCHO 24 ppm, R.H. 54%, total flow rate 50 cm^3/min).

Fig. 5. Dynamic changes of the in situ FT-IR spectra of the $Pt/TiO_2(A)C$ catalyst as a function of time in a flow of HCHO + N_2 + H_2O at room temperature (*Reaction conditions*: Inlet HCHO 24 ppm, R.H. 54%, total flow rate 50 cm^3/min).

Fig. 8. Decline in the CO_2 concentration with time after O_2 was shut off and H_2O was turned on over Pt/TiO$_2$(A)R catalyst (*Reaction conditions*: Inlet HCHO 22.2 ppm, 21% O_2/N$_2$, temperature 25 °C, R.H. 54%, S.V. 60,000 h^{-1}).

during the reaction. When this was carried out, CO_2 rapidly increased because of the oxidation of formaldehyde. In other words, 100% of the formaldehyde was removed even in the N_2 + HCHO + H_2O reaction, which contained no oxygen. Therefore, in order to understand the state of the hydroxyl group on the catalyst's surface at each stage in the H_2O pulse injection experiment,

the O1s peak was analyzed using XPS analysis (Fig. 9). In a typical O1s peak, the Ti–O on the surface appeared at 529.9 eV, the H_2O adsorbed physically or the –OH group appeared at 531.6 eV, and the C–O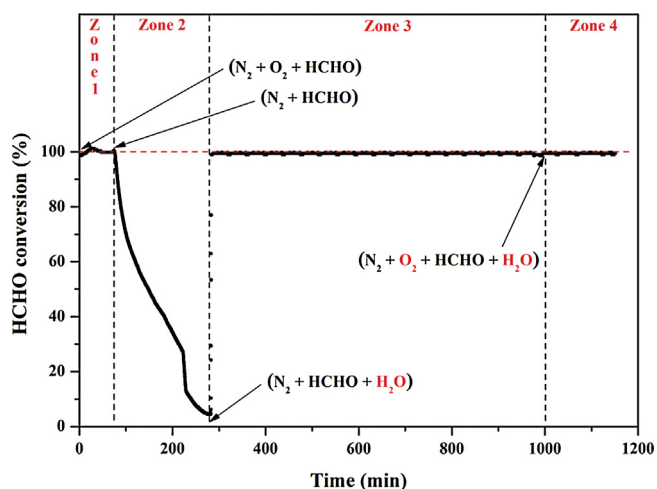 bond appeared at 532.2 eV [30]; these were divided into lattice oxygen and adsorbed oxygen so that the peak at 529.0 eV was O^{2-} from the lattice oxygen of Ti–O and the peak at 531.0 eV represented surface adsorbed oxygen, such as CO_3^{2-} or –OH, etc. [31]. Fig. 9(b) shows the O1s peak after the N_2 + HCHO reaction was separated. In this experiment, the –OH group on the surface was decreased compared with the result for the fresh catalyst. However, it is plausible that the –OH group was again recovered for the catalyst after the N_2 + HCHO + H_2O reaction. This process is more clearly demonstrated in Table 2, which shows the % area occupied by each peak, which was found to separate the O1s peaks at each stage in the H_2O pulse experiment. Meanwhile, Fig. 10 shows the result of the H_2O pulse injection experiment for the Pt/TiO$_2$(B)R catalyst at room temperature. In these experiments, the formaldehyde to CO_2 conversion was very low in the N_2 + O_2 + HCHO reaction. In addition, it was shown that the removal activity of formaldehyde was 0% if N_2 + HCHO were injected, as in the above experiment. In this experiment, the formaldehyde was not removed, even in the N_2 + HCHO + H_2O reaction. This catalyst was shown to remove all formaldehyde when both atmospheric oxygen and H_2O were supplied. After separating the O1s peak of the catalyst for each process (Fig. 11), the atom % occupied by each peak was different from those of the Pt/TiO$_2$(A)R catalyst. While the Pt/TiO$_2$(A)R catalyst recovered the O–H peak after the N_2 + HCHO + H_2O reaction, the Pt/TiO$_2$(B)R catalyst did not recover the O–H peak completely. If
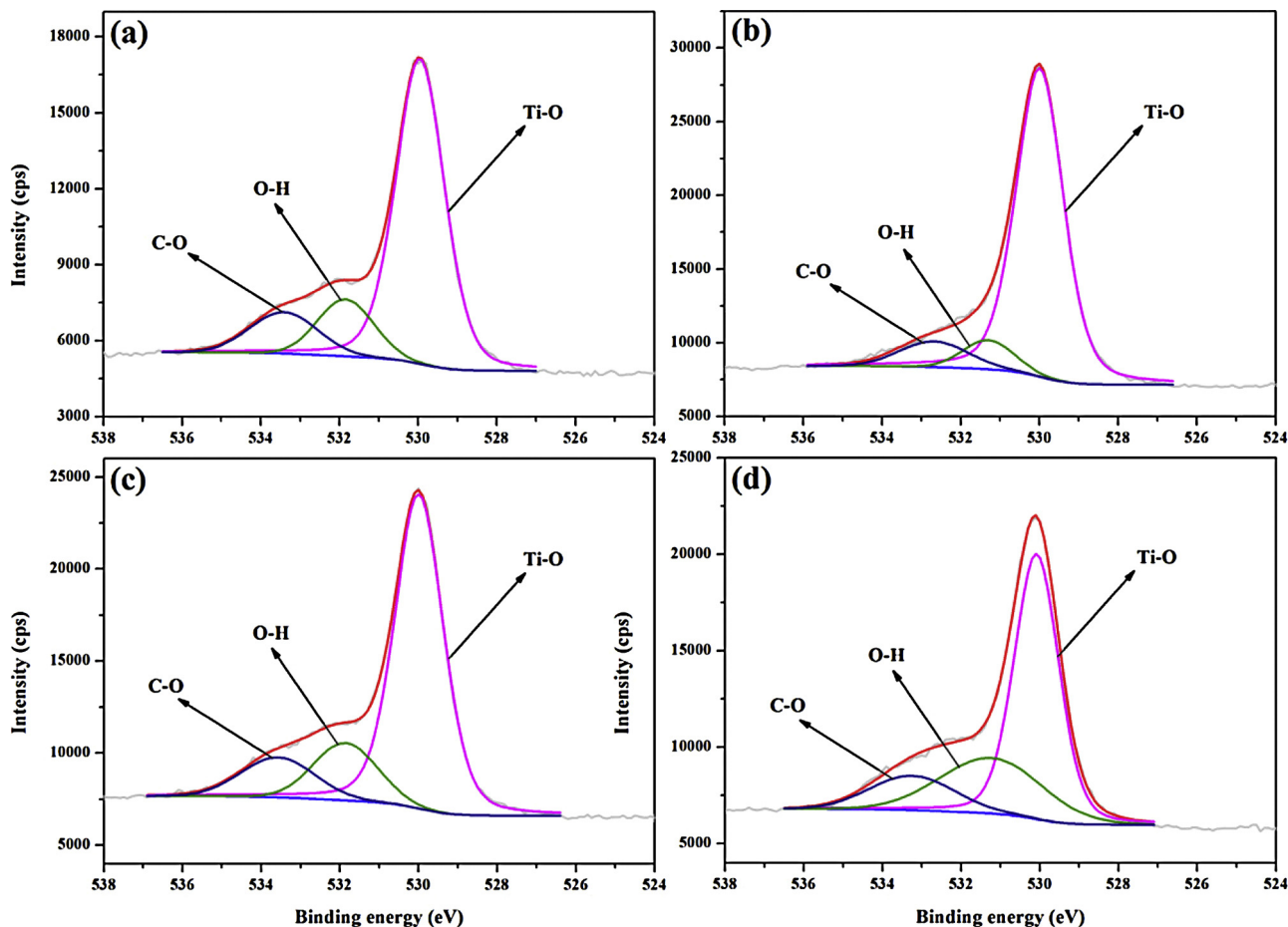
Fig. 9. XPS O1s spectra of the Pt/TiO$_2$(A)R catalyst: (a) zone 1, (b) zone 2, (c) zone 3 and (d) zone 4.

Table 2
Calculating the percent of the area between Ti–O, O–H and C–O in O1s of the Pt/TiO$_2$ catalysts by XPS.

Peak separation	Zone 1	Zone 2	Zone 3	Zone 4
Reduced Pt/TiO$_2$(A) catalyst				
Ti–O	73.5	83.6	72.3	63.5
O–H	14.1	7.5	15.4	22.7
C–O	12.4	8.9	12.3	13.8
Total	100	100	100	100
Reduced Pt/TiO$_2$(B) catalyst				
Ti–O	65.6	89.0	82.7	62.1
O–H	17.7	5.6	9.6	26.4
C–O	16.7	5.3	7.7	11.5
Total	100	100	100	100

Fig. 10. Decline in the CO_2 concentration with time after O_2 was shut off and H_2O was turned on over the Pt/TiO$_2$(B)R catalyst (*Reaction conditions*: Inlet HCHO 26.4 ppm, 21% O_2/N_2, temperature 25 °C, R.H. 54%, S.V. 60,000 h^{-1}).

both O_2 and H_2O were simultaneously supplied, the O–H peak of the fresh catalyst was recovered.

3.4. Effect of humidity on the Pt/TiO$_2$ catalysts prepared with various Pt loadings

Platinum catalysis is widely used for the addition or separation of hydrogen, as well as for oxidation [23–25,32,33]. However, the application of this catalyst is financially restricting because of the high cost of platinum. Recently, various studies have been conducted and are in progress that attempt to find ways of reducing the amount of platinum catalyst needed. Thus, in this section, formaldehyde oxidation experiments were performed with the goal of reducing the amount of platinum needed at room temperature. Table 3 shows the surface area and CO chemisorption properties of the Pt/TiO$_2$(A)R catalysts depending on Pt loading. CO chemisorption analysis of 0.01Pt/TiO$_2$(A)R catalyst is not measured since very low CO adsorption quantity. The surface area was increased with increasing Pt loading; the catalyst with 1 wt% Pt had the highest value. The metal dispersion tended to decrease.

Fig. 11. XPS O1s spectra of Pt/TiO$_2$(B)R catalyst: (a) zone 1, (b) zone 2, (c) zone 3 and (d) zone 4.

Table 3
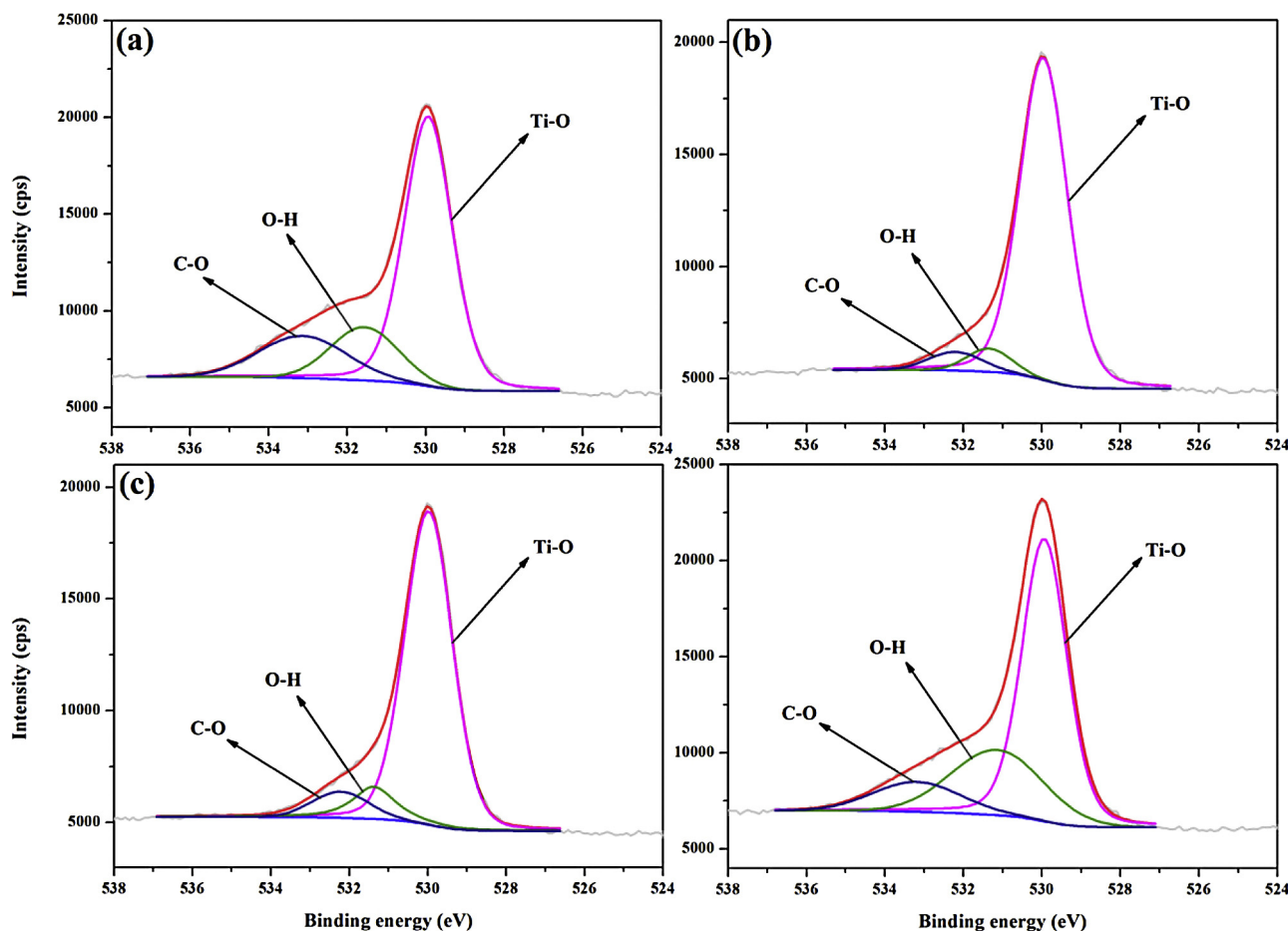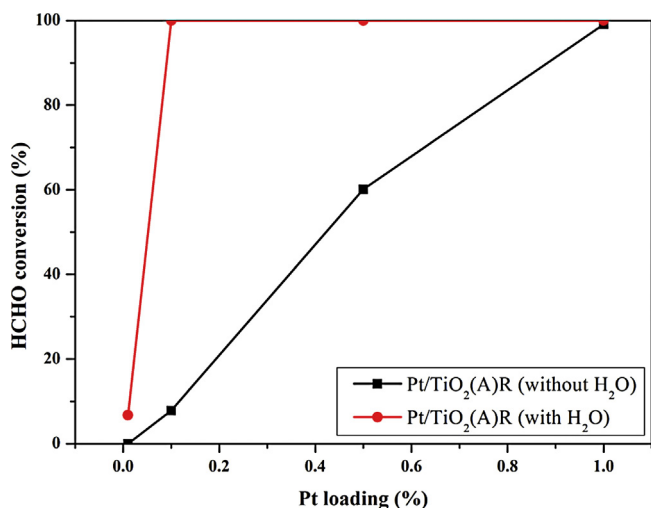The surface area and CO chemisorption properties of the Pt/TiO$_2$(A)R catalysts with different Pt loading.

Pt loading of Pt/TiO$_2$(A)R catalyst	S_{BET} (m^2/g)	Metal dispersion (%)	Metal surface area (m^2/g)	Active particle diameter (nm)
0.01Pt/TiO$_2$(A)R	42		Non-measured	
0.1Pt/TiO$_2$(A)R	51	72.87	18.00	1.55
0.5Pt/TiO$_2$(A)R	83	44.29	33.93	4.12
1Pt/TiO$_2$(A)R	107	35.38	47.88	10.63

Fig. 12. The effect of Pt loading on HCHO conversion over Pt/TiO$_2$(A)R (*Reaction conditions*: Inlet HCHO 24 ppm, 21% O$_2$/N$_2$, temperature 25 °C, R.H. 0 or 54%, S.V. 60,000 h^{-1}).

Conversely, the metal surface and the active particle diameter gradually increased. It was found that the Pt sites present on the catalyst surface were increased due to an increase in Pt loading. Fig. 12 shows the results of the formaldehyde oxidation experiment with platinum concentrations of 0.01–1.0%. In the presence of moisture, as shown in the results, most catalysts showed excellent activity even if platinum was loaded at a concentration of more than 0.5%. Additionally, 100% conversion of formaldehyde was observed even with a platinum concentration of 0.1%. The conversion of formaldehyde was reduced to 7% with a platinum concentration of 0.01%. Conversely, when there was no moisture, the conversion decreased rapidly with a platinum concentration of 0.5% and was 8% with a platinum concentration of 0.1%. To summarize, in this study, if moisture was present, the Pt/TiO$_2$ catalyst showed excellent formaldehyde oxidation activity with very low concentrations of platinum.

4. Conclusions

In this study, we examined the effect of relative humidity on HCHO oxidation at room temperature over Pt/TiO$_2$ catalysts. Based on the results of both the FT-IR experiments and the H$_2$O pulse injected experiments, the catalyst with excellent activity was shown to adsorb formaldehyde and convert it into formate (HCOO– or COO–) using surface –OH or lattice oxygen, even if atmospheric oxygen was not present. Adsorbed formate could be oxidized into CO$_2$ and H$_2$O using either surface –OH or –OH from H$_2$O. For applications of the Pt/TiO$_2$ catalyst in the presence of moisture, excellent activity was also shown with a very low platinum loading (0.1% of Pt).

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